Supporting Information

Self-assembly of Cerium-based Metal-Organic Tetrahedrons for Size-Selectively Luminescent Sensing Natural Saccharides

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1. Experimental Section.

1.1 Materials and Methods. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The elemental analyses of C, H and N were performed on a vario EL III elemental analyzer. $^1$H NMR spectra were measured on a BRUKER 400M spectrometer. ESI mass spectra were carried out on a HPLC-Q-Tof MS spectrometer using methanol as mobile phase. Uv-vis spectra were measured on a HP 8453 spectrometer. The fluorescent spectra were measured on EDINBURGH FS920. The emission quantum yield of the complexes was estimated with reference to quinine sulfate ($\Phi_f = 0.546$ in 1N sulfuric acid with excitation at 365 nm) $^{51}$ as the standard.

$$\Phi_{\text{unk}} = \Phi_{\text{std}} \left( \frac{I_{\text{unk}}}{I_{\text{std}}} \right) \left( \frac{A_{\text{unk}}}{A_{\text{std}}} \right) \left( \frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2$$

(1)

Where $\Phi_{\text{unk}}$ and $\Phi_{\text{std}}$ are the radiative quantum yields of the sample and standard, $I_{\text{unk}}$ and $I_{\text{std}}$ are the integrated emission intensities of the corrected spectra for the sample and standard, $A_{\text{unk}}$ and $A_{\text{std}}$ are the absorbance of the sample and standard at the excitation wavelength, and $\eta_{\text{unk}}$ and $\eta_{\text{std}}$ are the indices of refraction of the sample and standard solutions, respectively.

1.2 Preparation

2,6-naphthalene-dicarbohydrazide: A mixture solution of 80% hydrazine hydrate (40mmol, 2.50g) and dimethyl-2,6-naphthalene-dicarboxylate (4mmol, 0.86g) in methanol (20mL) was stirred over 12h. A white precipitate was formed, which was collected by filtration, washed with methanol and dried in vacuum. Yield: 0.80g, 82%.

$\text{H}_2\text{L}^1$: 2,6-naphthalene-dicarbohydrazide (3 mmol, 0.732g) was added to a CH$_3$OH solution (60 mL) containing salicylaldehyde (6.4 mmol, 0.781 g). After 5 drops of acetic acid was added, the yellow mixture was heated at boiling temperature under magnetic stirring for 24h. During the reaction, a pale yellow precipitate was formed, which was collected by filtration. Yield: 1.11g, 82%. Anal calc. for C$_{26}$H$_{20}$N$_4$O$_4$·2H$_2$O: H 4.95, C 63.93, N 11.47%. Found: H 4.90, C 64.00, N 11.16%. $^1$H NMR (DMSO-$d_6$,
ppm): 12.35(s, 2H_NH), 11.26(s, 2H_OH), 8.72(s, 2H_5), 8.65(s, 2H_8), 8.25(d, 2H_6, J = 8.4Hz), 8.10(d, 2H_7, J = 8.4Hz), 7.60(d, 2H_4, J = 6.8Hz), 7.33(t, 2H_2, J = 8.0Hz), 6.95(m, 2H_3, 2H_1).

**TE1:** A solution of Ce(NO_3)_3·6H_2O (8.4 mg, 0.02 mmol), H_2L^1 ligand (13.6 mg, 0.03mmol) and KOH (3.4 mg, 0.06 mmol) in CH_3OH/DMF (v:v = 1:7, 8 mL) was stirred for 2h. Then the solution was left for two weeks at room temperature to give X-ray quality black block crystals. Anal calc. for Ce_4(C_26H_18N_4O_4)_6·4C_3H_7NO·6H_2O·2CH_3OH: H 4.22, C 54.77, N 10.52%. Found: H 4.25, C 54.89, N 10.42 %. Yield: 65%.

**4,4'-biphenyl-dicarbohydrazide:** A mixture solution of 80% hydrazine hydrate (20mmol, 1.25g) and dimethyl-4,4'-biphenyl-dicarboxylate (2mmol, 0.49g) in methanol (20mL) was stirred over 12h. A white precipitate was formed, which was collected by filtration, washed with methanol and dried in vacuum. Yield: 0.43g, 80%

**H_2L^2:** 4,4'-biphenyl-dicarbohydrazide (3 mmol, 0.81g) was added to a CH_3OH solution (60 mL) containing salicylaldehyde (6.4 mmol, 0.78 g). After 5 drops of acetic acid was added, the yellow mixture was heated at boiling temperature under magnetic stirring for 24h. During the reaction, a pale yellow precipitate was formed, which was collected by filtration. Yield: 1.20g, 83%. Anal calc. for C_{28}H_{22}N_4O_4·0.5CH_3OH: H 4.89, C 69.22, N 11.33 %. Found: H 4.95, C 68.90, N 11.25%. ^1^H NMR (DMSO-^d_6, ppm): 12.21(s, 2H_NH), 11.30(s, 2H_OH), 8.69(s, 2H_5), 8.09(d, 2H_6, J = 8.4Hz)), 7.97(d, 2H_7, J = 8.4Hz), 7.57(d, 2H_4, J = 6.4Hz), 7.32(t, 2H_2, J = 8.0Hz), 6.95(m, 2H_3, 2H_1).

**TE2:** A solution of Ce(NO_3)_3·6H_2O (8.4 mg, 0.02 mmol), H_2L^2 ligand (14.4 mg, 0.03mmol) and KOH (3.4 mg, 0.06 mmol) in CH_3OH/DMF (v:v = 1:7, 8 mL) was stirred for 2h. Then the solution was left for two weeks at room temperature to give crystalline solid. The solid were dried vacuum. Anal calc. for Ce_4(C_{28}H_{32}N_4O_4)_6·2C_3H_7NO·2H_2O: H 4.18, C 57.83, N 10.08 %. Found: H 4.25, C 58.37, N 10.32 %. Yield: 60%.

**Reference**

2. Crystallography:

Intensities of TE1 were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs. The structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares methods with SHELXTL version 5.1. Crystal data of TE1 C$_{170}$H$_{156}$Ce$_4$N$_{28}$O$_{36}$, $M = 3727.71$, monoclinic, space group P2$_1$/n, black block, $a = 24.009$ (1), $b = 37.450$ (1), $c = 24.065$ (1) Å, $β = 92.650(2)^\circ$, $V = 21614$ (1) Å$^3$, $Z = 4$, $D_c = 1.146$ g cm$^{-3}$, $μ$(Mo-Kα) = 0.891 mm$^{-1}$, $T = 180(2)$ K. 31778 unique reflections [$R$int = 0.1333]. Final $R_I$ [with $I > 2\sigma(I)$] = 0.0849, $wR_2$(all data) = 0.1991 for $2\theta = 47^\circ$. CCDC number 705880.

In the structural refinement of TE1, non-hydrogen atoms, except the disordered solvent molecules were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms, whereas no hydrogen atoms corresponding to the disordered solvent molecules were added and refined. To assist the stability of refinements, several restraints were applied: (1) Four of the six naphthalene rings, seven of the twelve benzene rings and one hydroxyl oxygen atom were disordered into two parts. Except two of the benzene rings were refined as free variables, the others were refined with the site occupancy factors (s.o.f.) being fixed at 0.5. (2) For all the disordered rings, the geometrical constraints of idealized regular polygons were used, the C–C bond distance of the phenyl ring being 1.39 Å and the diagonal C–C distance of the phenyl ring being 2.78 Å. (3) thermal parameters on adjacent atoms in the disordered moieties were restrained to be similar. (4) Several partially occupied solvent molecules were disordered with the s.o.f. being fixed at suitable value. On the checkcif report, the short interatom separations are due to the disorder of corresponding solvent molecules.
3. **Figure S1** ESI-MS of **TE1** (top) and **TE2** (Bottom) in DMF/CH$_3$OH in present of KOH (0.1mM). The insert exhibits the measured and simulated isotopic patterns at 1097.45 (for **TE1**) and 1137.19 (for **TE2**) respectively.
4. **Figure S2** Molecular structure of the tetrahedron in **TE1**, including the disordered parts of ligands. The hydrogen atoms and solvent molecules were omitted for clarity.
5. **Figure S3** The coordination configuration of the Ce(1) centre in TE1. The bond lengths (Å) and angles (°) of the Ce(1) centre: Ce(1)–O(1) 2.229(3), Ce(1)–O(2) 2.414(4), Ce(1)–O(15) 2.412(4), Ce(1)–O(16) 2.224(4), Ce(1)–O(17) 2.212(4), Ce(1)–O(18) 2.448(4), Ce(1)–N(1) 2.595(5), Ce(1)–N(16) 2.607(5), Ce(1)–N(17) 2.687(4); O(17)–Ce(1)–O(16) 84.6(2), O(17)–Ce(1)–O(1) 86.6(2), O(16)–Ce(1)–O(1) 85.5(1), O(17)–Ce(1)–O(2) 86.0(2), O(16)–Ce(1)–O(2) 141.8(1), O(1)–Ce(1)–O(2), 130.5(1), O(17)–Ce(1)–O(15) 143.8(2), O(16)–Ce(1)–O(15) 130.1(2), O(1)–Ce(1)–O(15) 83.8(1), O(2)–Ce(1)–O(15) 74.3(1), O(17)–Ce(1)–O(18) 129.7(2), O(16)–Ce(1)–O(18) 88.4(1), O(1)–Ce(1)–O(18) 142.2(1), O(2)–Ce(1)–O(18) 70.6(1), O(15)–Ce(1)–O(18) 72.1(1), O(17)–Ce(1)–N(1) 76.1(2), O(16)–Ce(1)–N(1) 148.2(2), O(1)–Ce(1)–N(1) 69.3(2), O(2)–Ce(1)–N(1) 61.4(1), O(15)–Ce(1)–N(1) 67.8(2), O(18)–Ce(1)–N(1) 123.4(2), O(17)–Ce(1)–N(16) 150.2(2), O(16)–Ce(1)–N(16) 68.8(2), O(1)–Ce(1)–N(16) 80.5(2), O(2)–Ce(1)–N(16) 122.6(2), O(15)–Ce(1)–N(16) 61.4(2), O(18)–Ce(1)–N(16) 62.6(1), N(1)–Ce(1)–N(16) 122.9(2), O(17)–Ce(1)–N(17) 67.1(1), O(16)–Ce(1)–N(17) 76.1(1), O(1)–Ce(1)–N(17) 149.2(2), O(2)–Ce(1)–N(17) 65.9(1), O(15)–Ce(1)–N(17) 127.0(1), O(18)–Ce(1)–N(17) 62.7(1), N(1)–Ce(1)–N(17) 116.4(2), N(16)–Ce(1)–N(17) 114.3(1).
6. Figure S4 The coordination configuration of the Ce(2) centre in TE1. The bond lengths (Å) and angles (°) of the Ce(2) centre: Ce(2)–O(3) 2.317(4), Ce(2)–O(4) 2.230(4), Ce(2)–O(5) 2.187(3), Ce(2)–O(6) 2.445(4), Ce(2)–O(21) 2.167(4), Ce(2)–O(22) 2.491(4), Ce(2)–N(4) 2.594(5), Ce(2)–N(5) 2.674(5), Ce(2)–N(21) 2.614(5); O(21)–Ce(2)–O(5) 84.6(2), O(21)–Ce(2)–O(4) 87.0(2), O(5)–Ce(2)–O(4) 85.5(1), O(21)–Ce(2)–O(3) 85.9(2), O(5)–Ce(2)–O(3) 140.0(1), O(4)–Ce(2)–O(3) 132.8(1), O(21)–Ce(2)–O(6) 143.5(2), O(5)–Ce(2)–O(6) 129.2(1), O(4)–Ce(2)–O(6) 83.5(1), O(3)–Ce(2)–O(6) 75.4(1), O(21)–Ce(2)–O(22) 128.7(1), O(5)–Ce(2)–O(22) 87.1(1), O(4)–Ce(2)–O(22) 142.6(1), O(3)–Ce(2)–O(22) 69.2(1), O(6)–Ce(2)–O(22) 73.3(1), O(21)–Ce(2)–N(4) 77.1(2), O(5)–Ce(2)–N(4) 150.8(2), O(4)–Ce(2)–N(4) 71.2(2), O(3)–Ce(2)–N(4) 61.7(1), O(6)–Ce(2)–N4 66.5(2), O(22)–Ce(2)–N(4) 122.1(2), O(21)–Ce(2)–N(21) 69.7(1), O(5)–Ce(2)–N(21) 75.5(1), O(4)–Ce(2)–N(21) 150.8(2), O(3)–Ce(2)–N(21) 64.8(1), O(6)–Ce(2)–N(21) 125.7(1), O(22)–Ce(2)–N(21) 59.2(1), N(4)–Ce(2)–N(21) 117.8(2), O(21)–Ce(2)–N(5) 150.6(2), O(5)–Ce(2)–N(5) 69.0(2), O(4)–Ce(2)–N(5) 78.3(2), O(3)–Ce(2)–N(5) 122.7(2), O(6)–Ce(2)–N(5) 60.2(1), O(22)–Ce(2)–N(5) 64.8(1), N(4)–Ce(2)–N(5) 120.5(2), N(21)–Ce(2)–N(5) 113.7(2).
The coordination configuration of the Ce(3) centre in TE1, the disordered O(13') atom was omitted.

The bond lengths and angles of the Ce(3) centre: Ce(3)–O(11) 2.357(4), Ce(3)–O(12) 2.221(5), Ce(3)–O(13) 2.126(8), Ce(3)–O(13') 2.335(8), Ce(3)–O(14) 2.437(4), Ce(3)–O(23) 2.374(4), Ce(3)–O(24) 2.160(3), Ce(3)–N(12) 2.612(6), Ce(3)–N(13) 2.561(6), Ce(3)–N(24) 2.644(5); O(24)–Ce(3)–O(13) 87.7(2), O(24)–Ce(3)–O(12) 85.0(2), O(13)–Ce(3)–O(12) 77.3(3), O(24)–Ce(3)–O(13') 76.8(2), O(12)–Ce(3)–O(13') 89.1(2), O(24)–Ce(3)–O(11) 140.7(2), O(13)–Ce(3)–O(11) 88.1(3), O(12)–Ce(3)–O(11) 131.8(2), O(13')–Ce(3)–O(11) 88.8(2), O(24)–Ce(3)–O(23) 129.9(2), O(13)–Ce(3)–O(23) 135.8(2), O(12)–Ce(3)–O(23) 83.3(2), O(13')–Ce(3)–O(23) 151.0(2), O(11)–Ce(3)–O(23) 75.9(2), O(24)–Ce(3)–O(14) 89.2(2), O(13)–Ce(3)–O(14) 136.0(6), O(12)–Ce(3)–O(14) 146.0(1), O(13')–Ce(3)–O(14) 122.0(2), O(11)–Ce(3)–O(14) 67.7(2), O(23)–Ce(3)–O(14) 75.0(2), O(24)–Ce(3)–N(13) 73.3(2), O(13)–Ce(3)–N(13) 76.1(3), O(12)–Ce(3)–N(13) 146.0(2), O(13')–Ce(3)–N(13) 61.0(2), O(11)–Ce(3)–N(13) 67.8(2), O(23)–Ce(3)–N(13) 130.6(2), O(14)–Ce(3)–N(13) 61.0(2), O(24)–Ce(3)–N(12) 146.6(2), O(13)–Ce(3)–N(12) 66.6(3), O(12)–Ce(3)–N(12) 69.4(2), O(13')–Ce(3)–N(12) 81.7(2), O(11)–Ce(3)–N(12) 62.7(3), O(23)–Ce(3)–N(12) 69.5(2), O(14)–Ce(3)–N(12) 124.0(2), N(13)–Ce(3)–N(12) 117.3(2), O(24)–Ce(3)–N(24) 65.5(2), O(13)–Ce(3)–N(24) 147.7(2), O(12)–Ce(3)–N(24) 82.6(2), O(13')–Ce(3)–N(24) 141.8(2), O(11)–Ce(3)–N(24) 122.9(2), O(23)–Ce(3)–N(24) 64.8(1), O(14)–Ce(3)–N(24) 64.7(2), N(13)–Ce(3)–N(24) 110.2(2), N(12)–Ce(3)–N(24) 128.4(2).
**Figure S6** The coordination configuration of the Ce(4) centre in TEI. The bond lengths and angles of the Ce(4) centre: Ce(4)–O(8) 2.159(4), Ce(4)–O(20) 2.189(3), Ce(4)–O(9) 2.238(4), Ce(4)–O(10) 2.379(4), Ce(4)–O(19) 2.395(4), Ce(4)–O(7) 2.481(4), Ce(4)–N(8) 2.622(5), Ce(4)–N(20) 2.656(5), Ce(4)–N(9) 2.660(5); O(8)–Ce(4)–O(20) 85.4(2), O(8)–Ce(4)–O(9) 84.6(2), O(20)–Ce(4)–O(9) 88.0(1), O(8)–Ce(4)–O(10) 88.1(2), O(20)–Ce(4)–O(10) 139.3(2), O(9)–Ce(4)–O(10) 131.3(1), O(8)–Ce(4)–O(19) 142.1(2), O(20)–Ce(4)–O(19) 129.6(1), O(9)–Ce(4)–O(19) 83.2(2), O(10)–Ce(4)–O(19) 73.8(1), O(8)–Ce(4)–O(7) 129.5(2), O(20)–Ce(4)–O(7) 84.4(1), O(9)–Ce(4)–O(7) 144.1(1), O(10)–Ce(4)–O(7) 69.2(1), O(19)–Ce(4)–O(7) 75.2(1), O(8)–Ce(4)–N(8) 68.4(2), O(20)–Ce(4)–N(8) 76.2(2), O(9)–Ce(4)–N(8) 149.5(2), O(10)–Ce(4)–N(8) 64.1(2), O(19)–Ce(4)–N(8) 127.0(2), O(7)–Ce(4)–N(8) 61.0(1), O(8)–Ce(4)–N(20) 149.7(1), O(20)–Ce(4)–N(20) 68.5(1), O(9)–Ce(4)–N(20) 79.5(1), O(10)–Ce(4)–N(20) 121.6(1), O(19)–Ce(4)–N(20) 61.2(1), O(7)–Ce(4)–N(20) 65.0(1), N(8)–Ce(4)–N(20) 117.0(2), O(8)–Ce(4)–N(9) 76.6(2), O(20)–Ce(4)–N(9) 151.4(2), O(9)–Ce(4)–N(9) 68.5(1), O(10)–Ce(4)–N(9) 63.0(1), O(19)–Ce(4)–N(9) 65.5(1), O(7)–Ce(4)–N(9) 124.2(1), N(8)–Ce(4)–N(9) 116.2(2), N(20)–Ce(4)–N(9) 120.0(2).
9. **Figure S7** Plot of $\chi_M T$ vs. $T$ per tetrahedron for a polycrystalline sample of compound TE1.
10. **Figure S8.1** The Uv-vis absorption spectra of H$_2$L$_1$ (red line), TE1 (black line) in DMF/acetonitrile solution (15:85, v/v). For a comparison, here the molar absorptivity of TE1 is calculated as one sixth of the value of itself, corresponding to the number of ligands in the complex.

![Figure S8.1](image1.png)

**Figure S8.2** The family of the Uv-vis absorption spectra of H$_2$L$_2$ (red line), TE2 (black line). For a comparison, here the molar absorptivity of TE2 is calculated as one sixth of the value of itself, corresponding to the number of ligands in the complex.

![Figure S8.2](image2.png)
11. **Figure S9.1** Fluorescent spectrum of ligand $\text{H}_2\text{L}^1$ (50 $\mu$M, red line) and complex $\text{TE}1$ (50 $\mu$M, black line) in DMF/acetonitrile solution (15:85, v/v), excited at 360 nm.

![Fluorescent spectrum of ligand $\text{H}_2\text{L}^1$ and complex $\text{TE}1$.](image)

**Figure S9.2** Fluorescent response of ligand $\text{H}_2\text{L}^2$ (50 $\mu$M, red line) and complex $\text{TE}2$ (50 $\mu$M, black line) in DMF/acetone solution (5:95, v/v), excited at 320 nm.

![Fluorescent response of ligand $\text{H}_2\text{L}^2$ and complex $\text{TE}2$.](image)
12. **Figure S10** Family of UV-vis absorption spectra of TE1 in DMF/acetonitrile solution (15:85, v/v, 4 μM) upon the addition of various monosaccharides and disaccharides.
13. **Figure S11** Family of fluorescent spectra of TE1 in DMF/acetonitrile solution (15:85, v/v, 50µM) upon the addition of various monosaccharides and disaccharides, excited at 360 nm.
14. **Figure S12** Family of Uv-vis absorption spectra of TE2 (4 µM) in DMF/acetone solution (5:95, v/v) upon the addition of various monosaccharides and disaccharides.
15. **Figure S13** Family of fluorescent spectra of TE2 in DMF/acetone solution (5:95, v/v, 20μM) upon the addition of various monosaccharides and disaccharides, excited at 320 nm.
16. **Figure S14** Linear fit for \( \log\left(\frac{F-F_0}{F_L-F}\right) \) vs. \( \log[G] \) for corresponding titration curve of TE2.
17. Figure S15 XRD pattern of compound TE1 data (bottom) and simulation of the XRD according to single crystal diffraction of TE1 (top).